

Wasserstoffbrücken in kristallinen Onium-dimesylamiden: Drei *prim.*-Ammonium-dimesylamide mit zwei- oder dreidimensionalen Wasserstoffbrückenmustern

Polysulfonylamines, CXVIII [1]

Hydrogen Bonding in Crystalline Onium Dimesylamides: Three
prim.-Ammonium Dimesylamides Exhibiting Two- or Three-Dimensional
Hydrogen Bond Patterns

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Di(methanesulfonyl)amide, Primary Ammonium Cation, Crystal Structure,
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In order to study hydrogen bonding patterns in primary ammonium salts and the hydrogen bond acceptor potential of the dimesylamide anion, low-temperature X-ray structures have been determined for the 1:1 salts $\text{RNH}_3^+(\text{MeSO}_2)_2\text{N}^-$, where R = Et (**1**, monoclinic, space group $P2_1/n$, two independent formula units **A** and **B**) or 1-adamantyl (**2**, monoclinic, $P2_1/c$) and for the 1:2 salt $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]^{2+} \cdot 2 (\text{MeSO}_2)_2\text{N}^-$ (**3**, monoclinic, $P2_1/n$, cation crystallographically centrosymmetric). The NH_3^+ donor groups form two-centre or three-centre hydrogen bonds to four (**B**) or three (**A**, **2**, **3**) adjacent anions, giving rise to fundamentally different networks. The crystal packing of **1** displays a three-dimensional system of eight independent H bonds and may be viewed as a commensurate ionic self-clathrate, in which finite (**A**)₂ cyclodimers are inserted as guest entities into parallel tunnels between infinite (**B**)_∞ tapes. In contrast, owing to the steric demands of the 1-adamantyl group, compound **2** merely exhibits a two-dimensional pattern constructed from four independent H bonds and leading to cation-anion sheets. In the packing of **3**, two crystallographically independent H bonds generate a tape substructure of cations and anions in the ratio 1:2; these tapes are cross-linked into a three-dimensional network *via* a third independent H bond. In each of the structures, short C–H⋯A contacts (A = N⁻ and/or O) with H⋯A ≤ 260 pm and C–H⋯A ≥ 130° are observed.